PB-225 142/9

EVALUATION OF FLAME EMISSION DETERMINATION OF PHOSPHORUS IN WATER

William Rudolf Seitz

National Environmental Research Center

Prepared for:

Environmental Protection Agency

August 1973

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB-225 142/9

W74-01116

SELECTED WATER RESOURCES ABSTRACTS

INPUT TRANSACTION FORM

4. Title **EVALUATION OF FLAME EMISSION DETERMINATION OF PHOSPHORUS IN WATER,**

7. Author(s)

Seitz, W. ~~Rudolf~~

8. Organization

~~U. S.~~ Environmental Protection Agency, Athens, Georgia, Southeast Environmental Research Laboratory ~~Athens, Georgia 30601~~

10. EPA No. RAOP 16ADN-31

11. Contract/Grant No.

13. Type of Report and Period Covered

15. Supplementary Notes

Environmental Protection Agency, ~~Environmental~~ Technology Series Report ~~Number~~, EPA-660-2-73-007, August 1973. 18p, 4 fig, 2 tab, 18 ref.

16. Abstract

NUCOR's flame spectrometer for phosphorus analysis was evaluated. Response to phosphorus in the form of H_3PO_4 was linear from 3 µg/liter, the detection limit, to 120 mg/liter, the highest concentration tested. Metal ions depress phosphorus emission and must be removed by cation exchange prior to analysis. High concentrations (≥5 mg/liter) of sulfur interfere positively. Volatile phosphorus compounds produce a larger signal for a given phosphorus concentration than nonvolatile compounds.

River water samples were spiked with inorganic and organic phosphorus and analyzed. The measured phosphorus concentrations were 10-25% lower in river water than in deionized water. (EPA)

Reproduced by
NATIONAL TECHNICAL INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

17a. Descriptors

***Phosphorus, *Phosphates, *Flame Photometry, Phosphorus Compounds, Organophosphorus Compounds, Inorganic Compounds, Analytical Techniques, *Spectrophotometry, *Pollutant identification**

17b. Identifiers

***Flame Emission, ~~Emission~~ Spectrometry**

660-2-73-007

Copy available from GPO Sup Doc as EP 1.23/4, $0.50 ; microfiche from NTIS as PB , [illegible] $1.45

17c. COWRR Field & Group **05A, 02K**

18. Availability

19. Security Class. (Report)

20. Security Class. (Page)

21. No. of Pages

22. Price

Send To:

**WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U S DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240**

Abstractor **W. Rudolf Seitz** Institution **EPA, Southeast Env. Res. Laboratory**

WRSIC 102 (REV. JUNE 1971)

25

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Monitoring, Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

W74-01116

324016

EPA-660/2-73-007
August, 1973

EVALUATION OF FLAME EMISSION DETERMINATION OF PHOSPHORUS IN WATER

by

William Rudolf Seitz
Southeast Environmental Research Laboratory
College Station Road
Athens, Georgia 30601

ROAP 16ADN-31
Program Element 1B1027

NATIONAL ENVIRONMENTAL RESEARCH CENTER
OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
CORVALLIS, OREGON 97330

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price 50 cents

ABSTRACT

NUCOR's flame spectrometer for phosphorus analysis was evaluated. Response to phosphorus in the form of H_3PO_4 was linear from 3 µg/liter, the detection limit, to 120 mg/liter, the highest concentration tested. Metal ions depress phosphorus emission and must be removed by cation exchange prior to analysis. High concentrations ($\geq$5 mg/liter) of sulfur interfere positively. Volatile phosphorus compounds produce a larger signal for a given phosphorus concentration than nonvolatile compounds.

River water samples were spiked with inorganic and organic phosphorus and analyzed. The measured phosphorus concentrations were 10-25% lower in river water than in deionized water.

CONTENTS

		Page
Abstract		ii
Acknowledgment		iv
Sections		
I	Conclusions	1
II	Recommendations	2
III	Introduction	3
IV	Experimental	4
V	Results and Discussion	7
VI	References	17

ACKNOWLEDGMENTS

George Yager should receive credit for expert plumbing assistance, running the quality control samples, and correctly diagnosing and eliminating the cause of frequent flameouts.

SECTION I

CONCLUSIONS

Flame emission spectrometry is suitable for determining dissolved phosphorus in natural waters if metal ions are first removed by treatment with a cation-exchange resin.

Total phosphorus analysis requires a method for solubilizing particulate phosphorus.

Sulfur is a possible interference in phosphorus determinations.

The spectrometer delivered to the EPA is not completely satisfactory for routine operation, because background and sensitivity drift with time.

SECTION II

RECOMMENDATIONS

The flame spectrometer should be modified to minimize drift in background and sensitivity.

A simple chemical procedure for solubilizing particulate phosphorus must be developed to make total phosphorus analysis possible.

SECTION III

INTRODUCTION

The total phosphorus concentration in a body of water is a measure important to studies of eutrophication (1). The standard method for total phosphorus is to convert all phosphorus to orthophosphate by wet acid digestion, followed by colorimetric determination of orthophosphate using the reaction with ammonium molybdate to form molybdophosphoric acid (2).

Flame emission spectrometry is a possible alternative method for total phosphorus that would not require conversion of all phosphorus to orthophosphate. In a cool hydrogen-air flame, phosphorus forms POH which emits a broad band spectrum peaking at 525 nm. (3). This emission is used to selectively detect phosphorus-containing gas chromatography effluents (4) and can also be used to measure phosphorus in detergents (5,6), lubricating oil (7) and rocks (8). However, the only reported method with sufficient sensitivity for phosphorus analysis in water requires a nebulization chamber heated to 900° C (9).

A flame emission spectrometer, built specifically for total phosphorus analysis in water by NUCOR Corporation under EPA contract, achieves the additional sensitivity needed for water analysis by ultrasonic nebulization to convert the sample to an aerosol, rather than pneumatic nebulization as in conventional flame spectrometry. With ion exchange pretreatment to remove interfering cations, the spectrometer successfully measures dissolved phosphorus at concentrations likely to be found in nature. It does not respond to particulate phosphate.

SECTION IV

EXPERIMENTAL

SPECTROMETER

The flame emission spectrometer is described in detail in the final report for the contract between NUCOR Corporation and the EPA (10). The essential components of the spectrometer are an air-cooled burner, an interference filter to selectively pass the emission at 525 nm, and a photomultiplier to measure emission intensity. The burner is separated into a flame chamber and an emission chamber by a 1 mm orifice. This confines the flame to an area not seen by the photomultiplier, thus reducing the flame's contribution to background light intensity.

Hydrogen is supplied directly to the burner. Air is drawn into the burner by using an air driven aspirator to create an area of reduced pressure downstream from the burner. Because both the hydrogen flow and the air flow through the burner are drawn into the area of reduced pressure, the flow of air to the burner varies inversely with hydrogen flow for a given aspirator setting.

The gas flow system on the spectrometer delivered by NUCOR was modified for the evaluation. House air was used to drive the aspirator and cool the burner because the compressor supplied by NUCOR was too noisy. The compressor could be used for field work. Hydrogen, aspirator air, and cooling air were all monitored by flowmeters controlled by needle valves. No attempt was made to measure air flow to the burner because inserting a flowmeter in the air line would reduce the flow rate.

The flame was lit by reducing the air flow to the aspirator, turning on a spark generator, and gradually increasing the hydrogen flow. Lighting of the flame is indicated by a characteristic "popping" sound accompanied by an increase in background signal. Immediately after the flame ignites, the air flow through the aspirator is increased to the normal operating level.

Throughout most of the evaluation, the flame went out spontaneously every 30-45 minutes except when the burner was unusually hot. This happened when enough

water vapor condensed in the burner to block the 0.31 cm i.d., 5 cm tube from the emission chamber to the aspirator. The problem was later corrected by enlarging the tube diameter.

NEBULIZER

Sample aerosol is generated ultrasonically by a Mistogen EN142 electronic nebulizer normally used for inhalation therapy. The aerosol is blown out through a flexible plastic tube reduced to 0.62 cm i.d. at the outlet. The outlet is aimed at the sample inlet port of the spectrometer and positioned 4 cm away. It is clamped onto a ringstand held rigidly in position. When the aspirator air is turned on in the spectrometer, aerosol is drawn into the burner.

The rate of aerosol generation varies from sample to sample (11). However, this does not affect observed emission intensity as long as the rate at which aerosol comes from the nebulizer exceeds the rate at which aerosol is drawn into the burner.

Sample can be added directly to the nebulizer (requiring 100-150 ml for aerosol generation), or it can be added to medication cups that fit into the nebulizer vessel, thus reducing the minimum sample requirement to 10 ml. Both the nebulizer vessel and the medication cups are plastic, which can lead to problems with phosphorus compounds that tend to adsorb on plastic.

PROCEDURES

Interference studies and calibrations of emission vs. phosphorus concentration were done by making standard additions to 250 ml of solution in the nebulizer vessel. The nebulizer vessel was calibrated by weighing out 250 grams of water. It was then used volumetrically.

Response to phosphorus in different compounds was measured and analytical quality control samples were analyzed using the medication cups.

Because 10-20 seconds are required for the aerosol to stabilize, the first 30 seconds of aerosol flow were blocked from the spectrometer by a paper towel. This led to sharper emission peaks and reduced the amount of

water collecting in the sample inlet through aerosol condensation. When drops form in the sample inlet, they must be removed by a paper towel so that the quantity of aerosol reaching the flame is not reduced. Sample cups can be exchanged readily and total time for one emission reading is approximately 60 seconds.

Phosphorus standards were prepared by weighing. Dilute standards, <25 mg/liter, were prepared fresh daily.

SECTION V

RESULTS AND DISCUSSION

FLAME CONDITIONS

Figure 1 shows phosphorus emission intensity and background intensity as a function of air flow through the aspirator for fixed hydrogen flows. At low flow rates increasing aspirator air flow increases the observed phosphorus emission, probably by drawing more aerosol into the flame. Above a certain flow rate, increasing the aspirator air leads to a decrease in phosphorus emission and a sharp increase in background. The decrease in phosphorus emission occurs because the flame is no longer hydrogen rich, the condition favoring POH emission (12, 13). Because air flow to the burner varies inversely with hydrogen flow, the optimum aspirator flow rate is greater for higher hydrogen flow rates.

Normal operating conditions were hydrogen flow 800-1000 cc/min., aspirator air 8-9 liters/minute and cooling air 1 liter/minute.

RESPONSE TO PHOSPHORUS

Emission intensity vs. phosphorus concentration is linear from 0.003 mg/liter, the detection limit, to 120 mg/liter, the highest concentration tested, for phosphorus in the form of H_3PO_4. Figure 2 shows raw data over the range 0-0.15 mg/liter.

The blank emission for deionized water is usually less than the background emission in the absence of aerosol. Increasing the hydrogen/air ratio increases the water blank relative to background.

Response to phosphorus is most sensitive immediately after the flame is first lighted, i.e. when the spectrometer is coolest. As the instrument warms up, the sensitivity for phosphorus decreases. At least 15 minutes warmup is necessary to achieve sufficient stability to perform an analysis.

Prolonged continuous operation of the spectrometer (over one hour) leads not only to a loss of sensitivity but

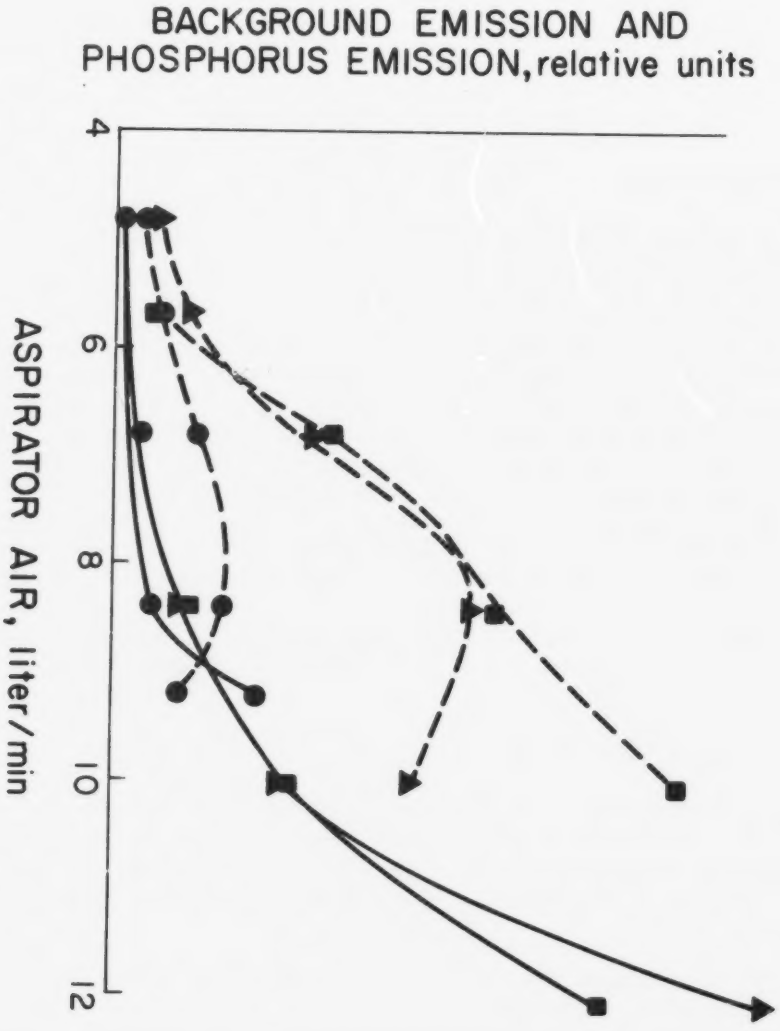


Figure 1. Effect of varying air flow through aspirator on phosphorus and background emission for fixed hydrogen flows

● - ● - ● Hydrogen flow 540 cc/min.

▲ - ▲ - ▲ Hydrogen flow 790 cc/min.

■ - ■ - ■ Hydrogen flow 1070 cc/min.

- - - - Phosphorus Emission

——— Background Emission

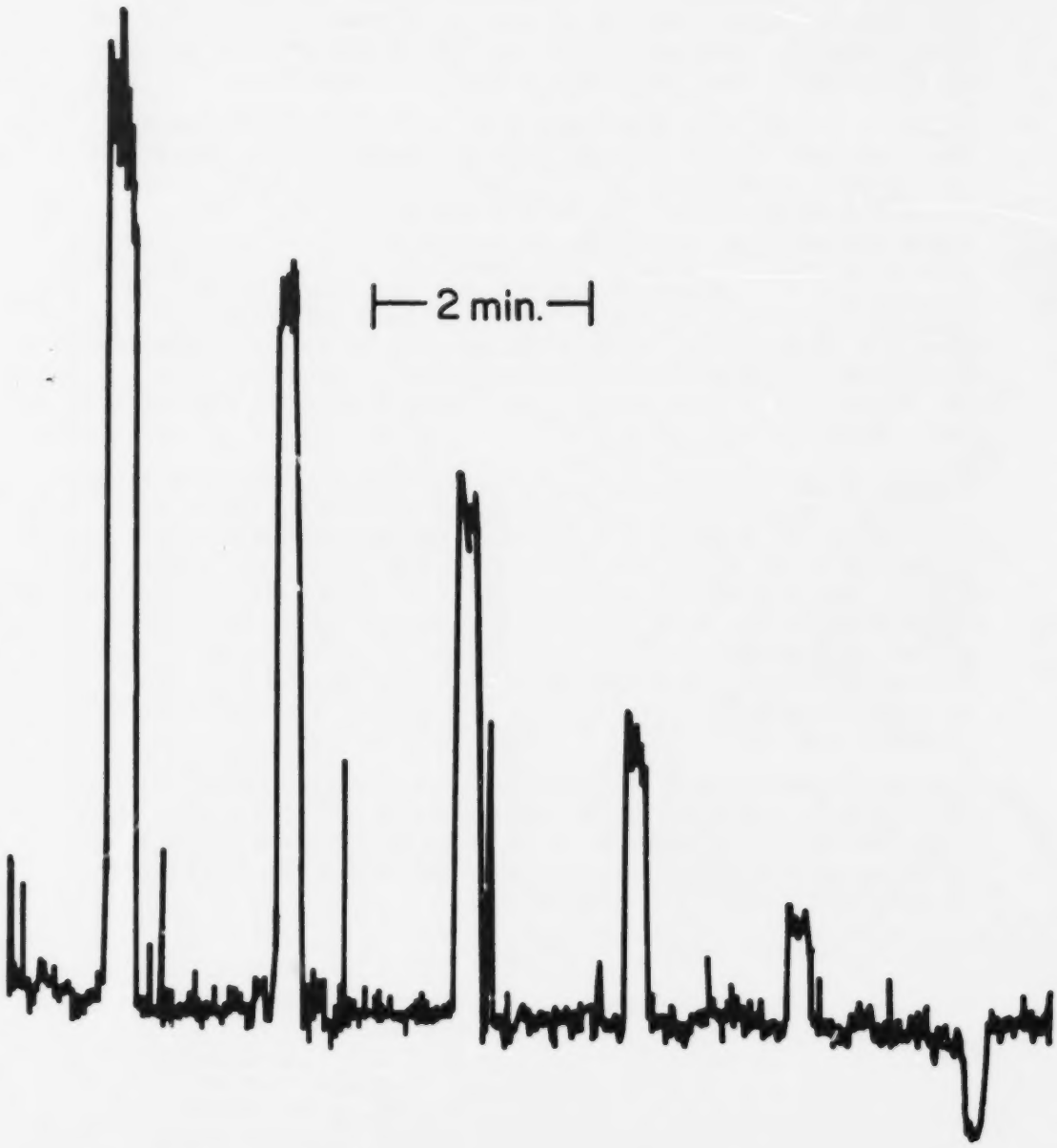


Figure 2. Raw data showing phosphorus emission as a function of concentration from 0 to 0.15 mg/liter in 0.03 mg/liter increments

also to a substantial increase in background. The background remains high when the flame is turned off, indicating that heating of the photomultiplier tube is responsible. Modification of the spectrometer design to eliminate this problem should be simple.

Table 1 lists relative emission per unit phosphorus for several phosphorus containing compounds. Volatile phosphorus compounds give a larger signal than non-volatile compounds. This is consistent with the observation that response to vapor phase triethyl phosphate is over 10 times more sensitive than the response to aqueous triethyl phosphate for the same amount of phosphorus reaching the flame per unit time (10). As aerosol evaporates in the flame, the volatile phosphorus compounds presumably vaporize sooner than the non-volatile compounds leading to more efficient excitation of POH emission.

A series of phosphorus-containing pesticides were to be run, but these compounds adsorbed on the plastic medication cups so rapidly that their phosphorus emission was impossible to measure satisfactorily. Of the compounds tried, only ruelene was stable. Triethyl thiophosphate adsorbed fairly rapidly, so the emission reading was taken immediately after the dilute solution was prepared. The medication cups used with adsorbing organic phosphorus compounds slowly desorbed phosphorus during subsequent use and had to be thrown out.

Because the organic compounds dissolved in natural waters are not likely to be volatile (14-16), the fact that volatile compounds give greater response per unit phosphorus is probably not a problem for phosphorus analysis in natural waters.

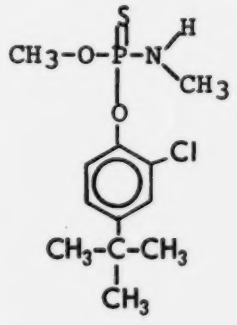
SULFUR INTERFERENCE

The hydrogen-air flame efficiently excites sulfur S_2 molecular emission peaking at 394 nm. (3,4,9,12,13). Some sulfur emission occurs at 525 nm, the wavelength of maximum phosphorus emission. Because two atoms produce one emitting S_2 molecule, emission intensity varies with the square of the sulfur concentration. Figure 3 plots the relative emission intensities for phosphorus and sulfur as a function of sulfur concentration. Above 5 mg/liter, sulfur rapidly becomes a significant interference.

Table 1. EMISSION INTENSITY PER UNIT PHOSPHORUS FOR DIFFERENT COMPOUNDS (relative to H_3PO_4)

Compound	Emission Intensity	Volatility
H_3PO_4	1.0	
$Na_4P_2O_7$	1.0	
Sodium glucose phosphate	1.0	
Ruelene*	1.3	
Triethyl phosphate	1.7	b.p. 215° 95°/10 mm
Triethyl thiophosphate	3.2	b.p. 100°/ 16 mm

*The structure of ruelene is



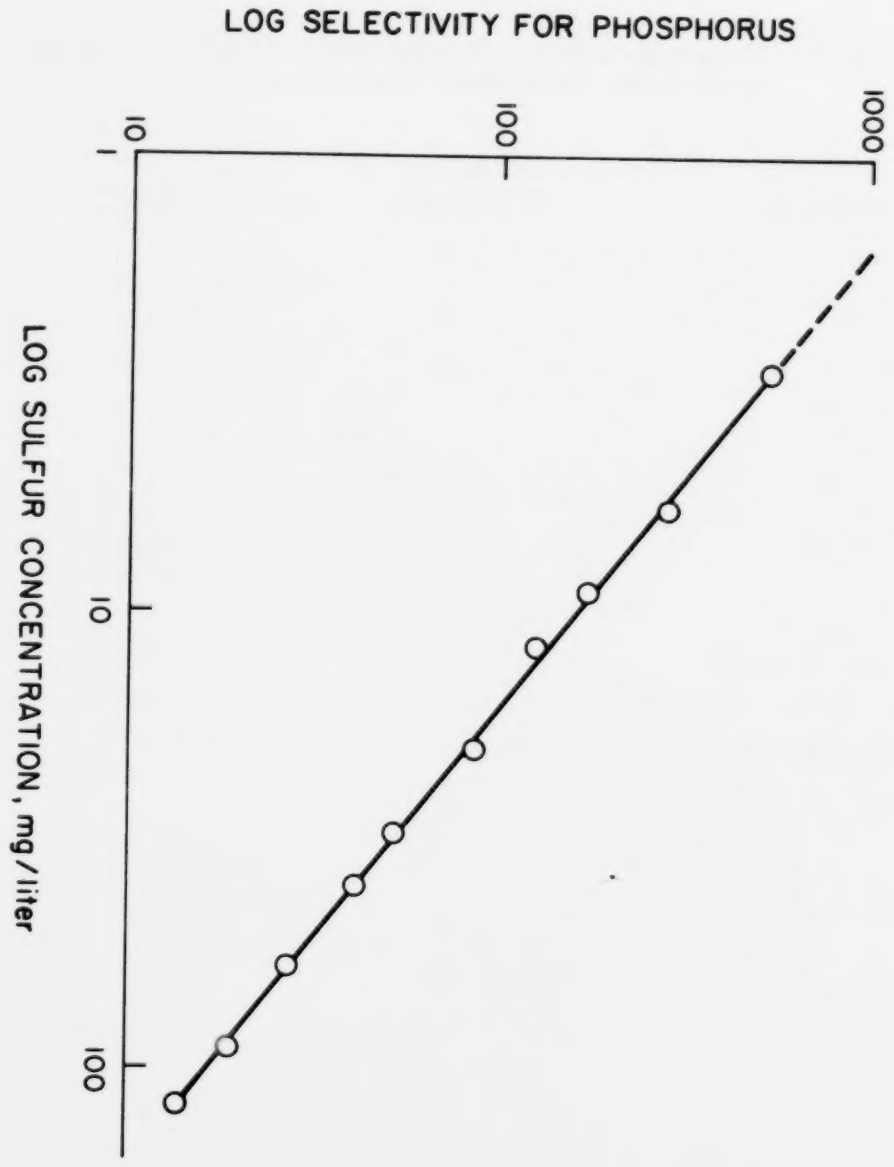


Figure 3. Selectivity of flame emission for phosphorus as a function of sulfur concentration. Selectivity is defined as

$$\frac{\text{emission/gm phosphorus}}{\text{emission/gm sulfur}}$$

If sulfur emission is suspected, its presence can be detected by diluting the sample to determine whether response is first or second order.

CATION INTERFERENCES

Cation depression of POH emission has been reported previously (5-9, 13). Figure 4 shows the effect of added Ca and Mg on phosphorus emission. Even Na and K depress phosphorus emission.

Interfering cations were removed by exposing a sample to 20-50 mesh Amberlite IR-120 strongly acidic cation exchange resin. Resin performance was tested using a column containing approximately five grams of resin. It was verified that passing deionized water through the column did not change the blank. One mg/l solutions of phosphorus in the form of H_3PO_4 and sodium glucose phosphate went through the column without any change in observed emission intensity. One mg/l phosphorus as H_3PO_4 in the presence of 100 mg/l each of Na, K, Ca and Mg went through the column with less than a 10% loss in emission intensity indicating that the column was satisfactorily removing interfering cations.

RIVER WATER ANALYSIS

To verify that flame emission analysis for phosphorus worked on river water samples, a series of analyses was performed on nutrient reference samples provided by EPA's Analytical Quality Control Laboratory, Cincinnati, Ohio. These samples are supplied as concentrates to be diluted by a factor of 200. Each sample type was diluted both in deionized water and in filtered river water. Samples 1 and 2 contain inorganic phosphorus and samples 3 and 4 contain organically bound phosphorus.

Passing river water through the cation exchange column resulted in losing the spike both for inorganic and organic phosphorus, even though no loss of phosphorus was observed in deionized water samples. If the ion exchange resin was added directly to the medication cup, it depressed the rate of aerosol generation. The procedure adopted was to add ion exchange resin to a liter of river water and shake it. This water was used for the river blank and the sample. The spiked river water was again treated with ion exchange resin to remove

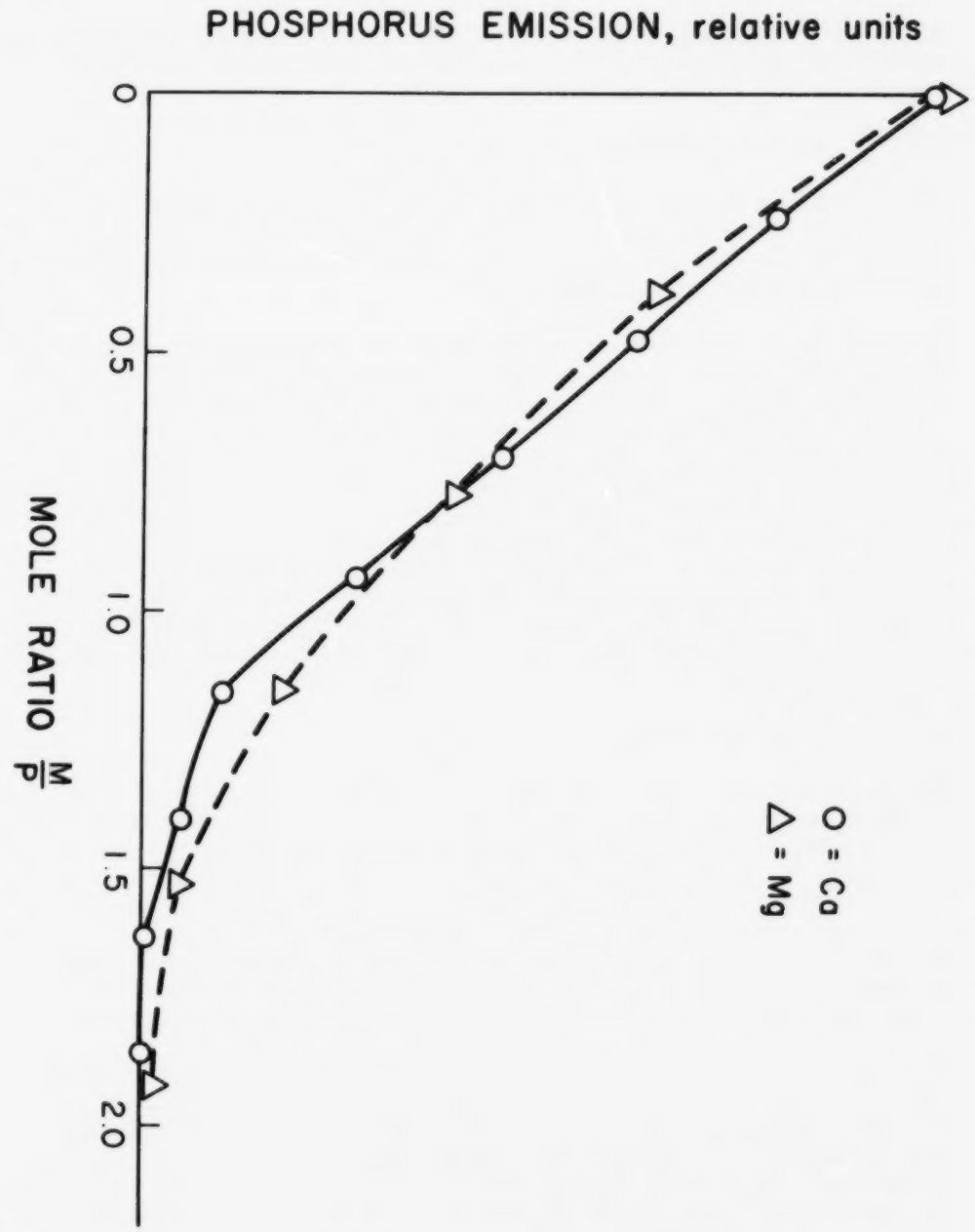


Figure 4. Effect of added calcium and magnesium ions on phosphorus emission

metal ions accompanying the spike. The spiking was done just before analysis so that the sample would not sit more than 10-15 minutes before being run.

Table 2 shows the results. The nominal concentration is given in the literature accompanying the quality control samples. The percentage recovery is the measured concentration of the spike in river water over the measured concentration of the spike in deionized water. Some of the spiked phosphorus is lost. I believe that it associates with particulate matter in the river water and is no longer available for excitation in the flame. This explanation is consistent with the known behavior of phosphate in natural waters (17-18). It may explain why the spike was lost using an ion exchange column, which would filter the sample.

From this behavior and the known susceptibility of the cool hydrogen-air flame to interference, it may be concluded that the flame does not possess sufficient thermal energy to break up particulate matter and excite particulate phosphorus emission.

The measured spike concentrations in deionized water agree with the nominal concentrations within 10%. Sources of variation in measured phosphorus concentration include:

- variations in sensitivity with time.
- differences in the quantity and droplet size of the aerosol with different solutions.
- uncertainties in peak intensity measurements.

Table 2. ANALYSIS RESULTS

Sample Number	Form of Phosphorus	Nominal conc. (mg/liter)	Measured Conc. Deion. H_2O (mg/liter)	Measured Conc. River Water (ppm) (mg/liter)	Percent Recovery	Source of River Water
1	Inorganic	-*	0.05*	0.038, 0.41 0.044	82%	Filtered Oconee River
2	Inorganic	0.300	0.28 0.27	0.22 0.21	78%	Filtered Oconee River
3	Organic	0.170	0.17 0.19	0.15 0.17	88%	Filtered Oconee River
4	Organic	0.85	0.79 0.83	0.69 0.69	85%	Filtered Oconee River

For samples 2, 3 and 4 the river water was run twice using separate samples. The same spiked deionized water was used for both measurements. The river water blank was equivalent to about 0.04 mg/l phosphorus.

* We ran out of quality control standard before arriving at a suitable analytical procedure. Data are for a synthetic standard.

SECTION VI

REFERENCES

1. Bartsch, A. F. Role of Phosphorus in Eutrophication. Environmental Protection Agency, Corvallis, Ore. Publication Number R3-72-001.

2. Standard Methods for the Examination of Water and Wastewater. 13th edition. American Public Health Association, 1971. p. 518-534.

3. B. Draeger, Heinrich Draegerwerk. West Germany Patent 1,133,918. July 26, 1962.

4. Brody, S. S., and J. E. Chaney. Flame Photometric Detector-Application of a Specific Detector for Phosphorus and for Sulfur Compounds. J Gas Chromatog. 4: 42-46, February 1966.

5. Syty, A. Determination of Phosphorus in Detergents by Flame Emission Spectrometry. Anal. Lett. 4: 531-536, August 1971.

6. Elliot, W. N., and R. A. Moslyn. The Determination of Phosphate in Detergents by Cool-Flame Emission Spectroscopy. Analyst (London). 96: 452-456, June 1971.

7. Elliott, W. N., C. Heathcote, and R. A. Moslyn. Determination of Phosphorus in Lubricating Oils by Cool-Flame Emission Spectroscopy. Talanta. 19: 359-363, 1972.

8. Syty, A. Determination of Phosphorus in Phosphate Rock by Cool Flame Emission Spectrometry. At. Absorption Newslett. 12: 1-2 January-February 1973.

9. Aldous, K. M., R. M. Dagnall, and T. S. West. The Flame-Spectroscopic Determination of Sulphur and Phosphorus in Organic and Aqueous Matrices by Using a Simple Filter Photometer. Analyst (London). 95: 417-424, May 1970.

10. NUCOR Corporation. Automated Water Monitoring Instrument for Phosphorus Contents. Final Report for EPA Contract No. 68-01-0111, 1973.

11. Stupar, J., and J. B. Dawson. Theoretical and Experimental Aspects of the Production of Aerosols for Use in Atomic Absorption Spectroscopy. Appl. Opt. 7: 1351-1358, July 1968.

12. Syty, A. and J. A. Dean. Determination of Phosphorus and Sulfur in Fuel-Rich Air-Hydrogen Flames. Appl. Opt. 7: 1331-1336, July 1968.

13. Dagnall, R. M., K. C. Thompson, and T. S. West. Molecular-Emission Spectroscopy in Cool Flames. Analyst (London). 93: 72-78, February 1968.

14. Gales, M. E., E. C. Julian, and R. C. Kroner. Method for Quantitative Determination of Total Phosphorus in Water. J. Am. Wat. Wks. Assoc. 58: 1363-1368, October 1966.

15. Fuhs, G. W. Determination of Particulate Phosphorus by Alkaline Persulfate Digestion. Intern. J. Environ Anal Chem. 1: 123-129, 1971.

16. Burton, J. K. Problems in the Analysis of Phosphorus Compounds. Water Research. 7: 291-307, 1973.

17. Chen, Y. S. R., J. N. Butler, and W. Stumm. Kinetic Study of Phosphate Reaction with Aluminum Oxide and Kaolinite. Environ. Sci Technol. 7: 327-332, April 1973.

18. Syers, J. K., R. F. Harris, and P. E. Armstrong. Phosphate Chemistry in Lake Sediments. J. Enviror Quality. 2: 1-14, January-March 1973.